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THE PYROLYSIS PRODUCTS AND THERMAL CHARACTERISTICS OF COTTONWOOD AND ITS COMPONENTS

Charles W. Philpot

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Ø 1-14
Charles W. Philpot

INTERMOUNTAIN FOREST AND RANGE EXPERIMENT STATION
Forest Service
U.S. Department of Agriculture
Ogden, Utah 84401
Robert W. Harris, Director

THE AUTHOR

CHARLES W. PHILPOT is a Research Forester in the Fire Physics research work unit at Missoula, Montana. His B.S. and M. S. degrees in Forestry were obtained in 1961 and 1962, respectively, from the University of California at Berkeley. He received his Ph.D. in Plant Science-Forestry in 1970 from the University of Montana. He was assigned to the Pacific Southwest Forest and Range Experiment Station at Berkeley from 1961 to 1963 and to the Riverside Forest Fire Laboratory in Riverside, California, from 1963 to 1966. In 1966 he transferred to Intermountain Station's Northern Forest Fire Laboratory at Missoula, where he initiated the first fuel chemistry studies. He has shown the chemical composition of plant materials, pyrolytic reactions, and the behavior of the extractives to be important in fire spread, intensity, and fuel ecology.

I wish to thank Professor F. Shafizadeh, Professor of Chemistry and Forestry, and Dr. G. McGinnis, Research Associate, both of the University of Montana, for their cooperation and help on this study.

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ABSTRACT

This study was undertaken to determine the thermal properties of, and the pyrolysis products from, western cottonwood (*Populus trichocarpa*) and two of its major components: cellulose and xylan. The modifications due to treatment of the wood and its components with an acid and alkali were also documented. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA), as well as direct pyrolysis into a temperature-programed gas-liquid chromatograph, were used in this investigation.

The components of cottonwood were found to generally behave the same in a thermal environment, both in isolated form and when combined in the whole wood. The hemicellulose, xylan, was completely pyrolyzed prior to the onset of cellulose pyrolysis. The acid salt treatment decreased pyrolysis rate of wood, cellulose, and xylan, and increased char, water, and furan compounds while decreasing the major two and three carbon fragments. The alkali treatment also decreased the pyrolysis rate and increased the production of char and water, but decreased the furan compounds while increasing the two and three carbon fragments.

INTRODUCTION

Fire is an integral part of the natural environment and a constant threat to man's surroundings. It has shaped the forests and grasslands and provided mankind with heat, power, and one of his most devastating weapons. In order to understand fire in its many potential roles we must determine the processes involved in conversion of fuels to volatile compounds, which in turn undergo combustion. An essential part of this process is the initial breakdown and pyrolytic reactions of fuel before it burns. This study was initiated, using modern chemical methods, to help lay the groundwork for research leading to the identification of these reactions.

This information will be helpful for coping with the many types of fires which are a major national problem. In the United States over 150,000 persons suffer nonfatal burns each year and it is estimated that 12,500 lives are lost in fires which represent a 5-billion dollar loss (Broido 1965). During 1966, a total of 2,396,550 fires of all types caused \$1,860,500,000 in property damage (National Fire Protective Association 1967). This included 970,000 building fires. During the same period, fires burned 4,574,389 acres of forest lands (USDA Forest Service 1967).

The majority of these fires involve wood and wood products, generally referred to as cellulosic fuels. Cellulosic fuels are not flammable as such, but in the presence of a sufficiently powerful source of ignition they undergo pyrolysis and produce volatile compounds which burn in the gas phase and result in the propagation of flaming combustion. The purpose of this study is to identify the major compounds resulting from the pyrolysis of cellulose, hemicellulose, and wood. With the addition of thermal analysis of these fuels, we hope to determine the interaction among the components undergoing pyrolysis. This should tell us whether studying the thermal properties of the components of wood is a valid technique for the study of the thermal properties of whole wood. Because knowledge of the pyrolysis mechanisms hopefully will lead to the design of efficient flame retardants, a portion of this study deals with the effect of zinc chloride and sodium hydroxide on the pyrolysis of wood and its components.

It is a difficult task to identify these major compounds because of the complex chemical composition of wood, which in addition to cellulose also contains hemicelluloses, lignin, extractives, ash (inorganics), and other extraneous materials. Furthermore, the pyrolysis processes generally involve many concurrent and consecutive reactions. Therefore, the only hope for identifying these mechanisms lies in a systematic approach involving analysis of a selected wood and its components and studying the pyrolytic behavior of each component individually and collectively.

Fire may be defined as the interaction of fuel, energy, and environment. The chemistry of fire deals with the interaction of fuel and energy and consists mainly of the pyrolytic reactions which lead to flaming combustion.

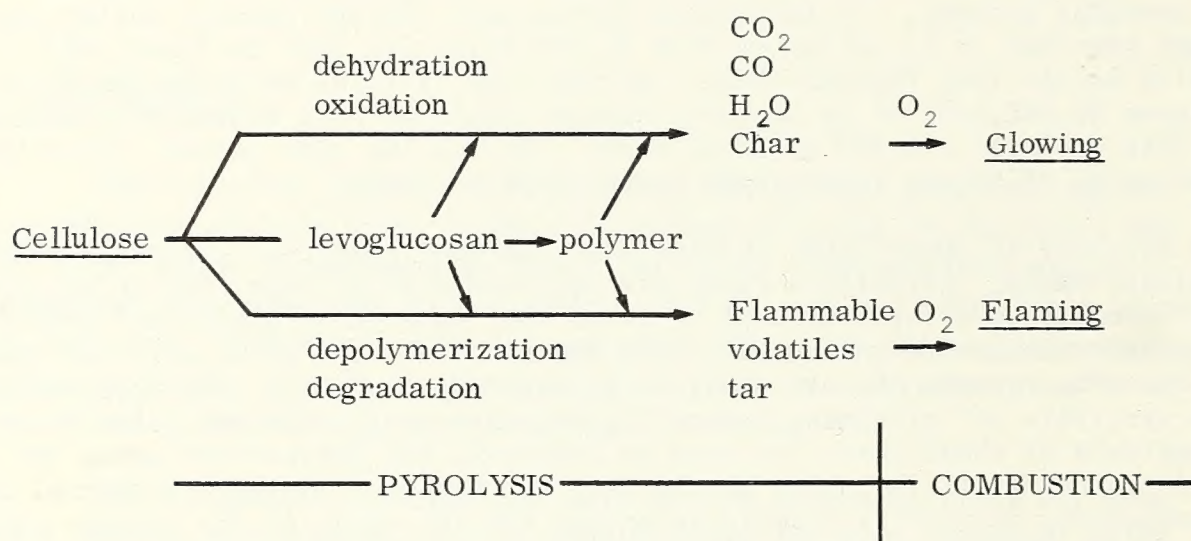
THE PYROLYSIS OF CELLULOSIC MATERIALS

The pyrolysis of cellulosic fuels has been recently reviewed by Shafizadeh (1968). This review covers a broad range of related subjects, including the historical background and the currently available information on the primary and secondary thermal reactions involved in the pyrolysis of cellulose.

Pyrolysis can be simply defined as the thermal degradation of a molecule into various products. The pyrolysis of cellulosic material is defined as the thermal degradation into volatile and nonvolatile products prior to combustion. This means it is usually isolated from combustion by performing experiments in an inert atmosphere or in vacuum. In general the pyrolysis products of wood and wood components are volatiles, tar, and char. The volatile products consist mainly of CO_2 , H_2O , various acids, and carbonyl compounds. The tar includes extractives and higher molecular weight degradation products. When cellulose is pyrolyzed, the major component of the tar is 1,6-anhydro- β -D-glucopyranose, commonly known as levoglucosan.

The tar from the xylan component of the hemicelluloses consists mostly of D-xylose dimers and trimers.¹ Char is the carbonaceous residue, the composition of which depends on the extent of pyrolysis.

The pyrolysis of cellulose can be represented graphically as follows:



At temperatures below 250° C. pyrolysis of cellulose occurs very slowly and the main products are CO_2 , CO , H_2O , and char. In the presence of O_2 the char could undergo localized surface oxidation or glowing. At temperatures above 320° C. pyrolysis occurs at a much faster rate and leads to the formation of levoglucosan and other volatile degradation products. In an oxygen atmosphere the combustible volatiles burn with flaming combustion. Levoglucosan follows the same sort of route² or forms a polymer which can likewise pyrolyze by the two routes.³ Preliminary work with 4-O-methylglucronoxylan (xylan) has shown this hemicellulose to have the same general action with the exception that no levoglucosan is formed.⁴ Levoglucosan has been considered as an intermediate pyrolysis product of cellulose and it has been shown that it could undergo the same type of charring and degradation reactions (Shafizadeh 1968, Ostojic,² and Shafizadeh and others³).

¹G. D. McGinnis. Pyrolysis of xylan and model compounds. 1970. (Unpublished Ph.D. Thesis on file at the Univ. of Mont., Missoula.)

²N. Ostojic. Pyrolysis of levoglucosan. 1970. (Unpublished master's thesis on file at the Univ. of Mont., Missoula.)

³F. Shafizadeh, C. W. Philpot, and N. Ostojic. Thermal analysis of 1,6- β -D-glucopyranose. USDA Forest Serv., Intermountain Forest and Range Exp. Station, Ogden, Utah 84401. (Manuscript in preparation.)

⁴McGinnis, op. cit.

The flame retardants enhance charring reactions at the expense of the degradation reactions which produce combustible volatile products.

PYROLYSIS PRODUCTS

A great variety of compounds have been identified among the destructive distillation products of wood and cellulose. Much less is known about the thermal decomposition products of the hemicellulose and lignin. The interest in the pyrolysis of wood originated from the commercial value of naval stores and the destructive distillation products, most of which have been replaced by other chemicals from alternate sources. In 1909 Klason and coworkers identified the products derived from the destructive distillation of cotton cellulose (Klason, Heidenstam, and Norlin 1909); these products are shown in the following tabulation.

<i>Products</i>	<i>Percent by weight</i>
Water	34.52
Acetic acid	1.39
Acetone	.07
Tar	4.18
Other organic compounds	5.14
Carbon dioxide	10.35
Carbon monoxide	4.15
Methane	.27
Ethylene	.17
Coke	38.82

Through subsequent research the following products were added to the list: methane formaldehyde; formic acid; acetone; butanone; glyoxal; glycoaldehyde; α -valerolactone; malthol; 2-furaldehyde (furfural); 5-(hydroxy methyl)-2-furaldehyde; methyl furan; 2,5-dimethyl furan; and tri- and tetramethyl furan (Shafizadeh 1968). Schwenker and Beck investigated the products derived from cellulose that were pyrolyzed directly into a gas-liquid chromatograph (Schwenker and Beck 1963). They reported the following major products: fixed gases; formaldehyde; acetaldehyde; water; propionaldehyde; acetone; acrolein; acetic acid; glyoxal; methanol; n-butyraldehyde; butanone; furfural; formic acid; lactic acid; and 5-(hydroxy-methyl)-2-furaldehyde.

Broido and Martin (1961) exposed cellulose sheets to intense irradiation levels of 4.4 to 11.6 cal. cm.⁻² sec.⁻¹ for 0.4 to 0.8 seconds. Using mass spectroscopy, they found the major products to be CO, CO₂, and lesser amounts of H₂, CH₄, C₂H₆, and C₃H₈ in the gases. The liquid phase contained mainly H₂O and small amounts of acetaldehyde, propionaldehyde, butyraldehyde, acrolein, crotonaldehyde, furan, acetone, butanedione, and methanol. The tar was found to be mostly levoglucosan.

Recently Lipska and Wodley (1968) have published the results obtained from a study of isothermal pyrolysis of cellulose in a fluidized bed. The volatile products were resolved with a gas liquid chromatograph (GLC) directly coupled to a mass spectrometer. Figure 1 shows a typical chromatogram from their work. Wodley (1969) has compiled a long list of products that so far have been identified from the pyrolysis of cellulose.

These data indicate that the qualitative and quantitative composition of the pyrolysis products could vary substantially according to the experimental pyrolysis conditions. The most significant variables are the temperature, ambient atmosphere, and the presence of various contaminants or impurities.

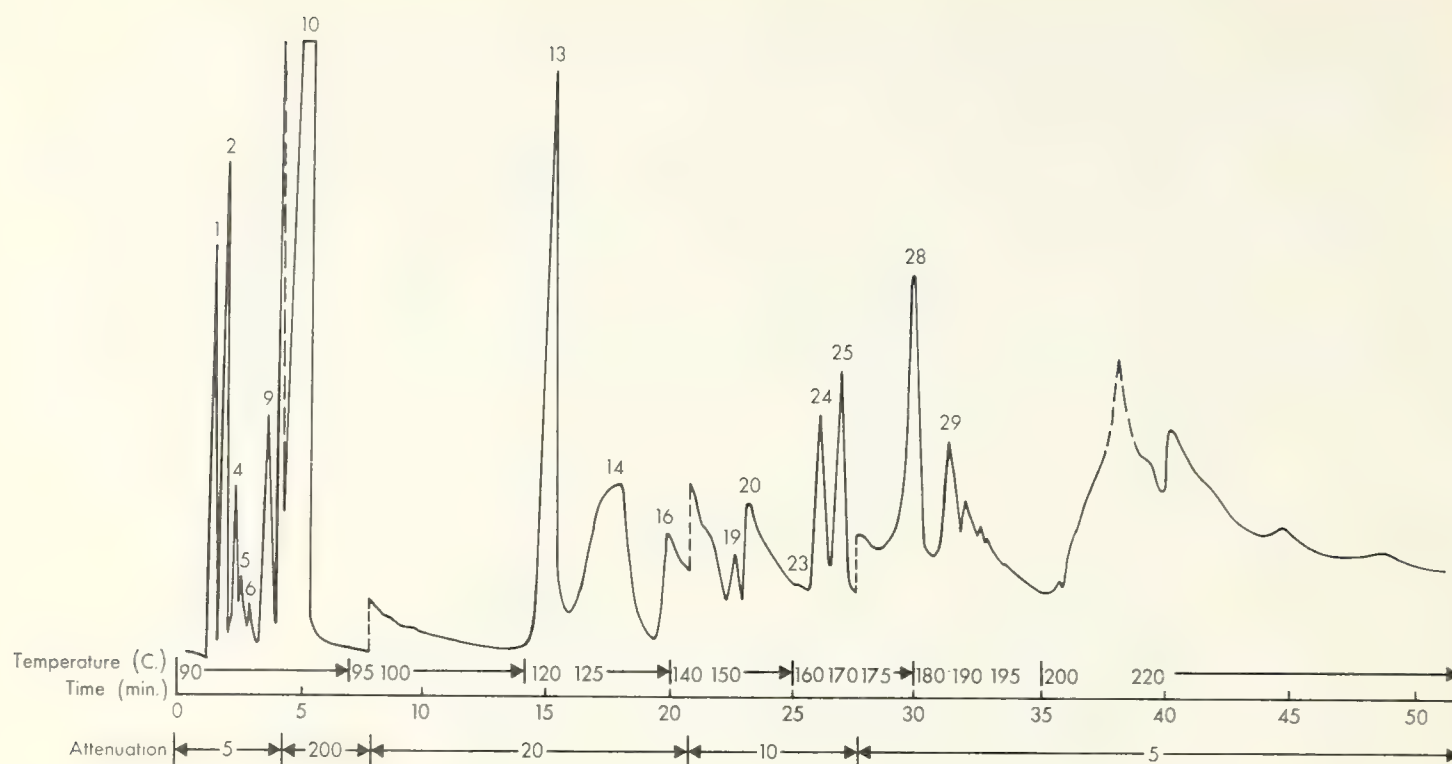


Figure 1.--Chromatogram of cellulose pyrolyzed at 300° C. (Lipska and Wodley 1968). The peaks are (1) fixed gases; (2) acetaldehyde; (4) furan; (5) propionaldehyde; (6) acetone; (9) 2,3-butanedione; (10) water; (13) acetol; (14) methyl formate +; (16) furfural +; (19) propionic acid; (20) formic acid; (23) acetic acid; (24) furfuryl alcohol; (25) butyrolactone; (28) cyclohexanone; and (29) tigaldehyde.

ISOLATION OF THE CHEMICAL COMPONENTS OF WESTERN COTTONWOOD

Western cottonwood (*Populus trichocarpa*) was selected for this study for several reasons. It is currently considered a low-grade western hardwood of little utility but may have future commercial value. The chemical investigations have been limited to certain commercial and biological aspects (Mehring and Schramm 1949; Butin 1960; Mojeika and Sergeera 1957). There has been some reported work dealing with the phenyl glucosides found in the bark (Loeschcke and Franchsen 1964; Pearl and Larson 1965) and some information has also been available on the polysaccharides of the related species, *Populus tremuloides* and *Populus grandidentata* (Jones, Purves, and Timell 1961; Thompson and Wise 1952). This work will greatly increase our knowledge about this potential raw material. Selection of western cottonwood simplifies the investigation procedures because hemicelluloses found in the plant consist mainly of xylan. Another advantage in using this wood is the low content of extraneous materials, especially ash. This helps insure isolation of the carbohydrates in a nearly pure form.

The chemical analysis and isolation of the polysaccharide component of cottonwood were carried out mainly by McGinnis⁵ and are reported elsewhere in more detail (Shafizadeh and McGinnis 1971). Further analysis of the inorganic materials was carried out by this author.

A heartwood sample of the cottonwood was analyzed to provide the cell wall polysaccharides and the other components shown in the following tabulation. Hydrolysis

⁵McGinnis, op. cit.

Table 1.--*Inorganic content of cottonwood and the isolated polysaccharide components*

Component	Ash	Ca	K	P	Fe	Na
----- Percent dry weight -----						
Wood	0.37	0.059	0.065	0.0122	0.0074	0.006
Extracted wood	.29	.058	.016	.0006	.0057	.006
Holocellulose	1.02	.020	.001	.0014	.0032	¹ .394
Cellulose	.15	.002	.002	.0003	.0063	.003
Base-extracted xylan	.15	.001	.001	.0003	.0060	.070
DMSO-extracted xylan	.41	--	--	--	--	--

¹Additions due to base extraction procedure.

of the polysaccharides (holocellulose component) to the sugars indicated the presence of cellulose, "xylan," and "mannan." These polysaccharides were isolated using the procedure of Jones and others (1961). This gave 42 percent cellulose, 18 percent 4-0-methylglucuronoxylan, and 4.1 percent glucomannan based on original wood substance.

Component	Percent of dry wood	Percent of extracted wood
Benzene-alcohol (2:1) soluble	7.4	
Alcohol soluble	.8	
Total extractives	8.2	
Klason lignin ⁶		31.9
Cell wall polysaccharides		76.1

The holocellulose fraction was also extracted with dimethyl sulfoxide (DMSO) to give a small yield of 0-acetyl-4-0-methylglucuronoxylan. This was used for the determination of acetyl groups, which are hydrolyzed under the alkaline condition of the systematic fractionation. Analysis of this product showed 9.9 percent acetyl content.

Hydrolysis of the "xylan" and analysis of the hydrolyzate showed the presence of D-xylose and only a trace of D-glucose impurities. However, as usual, no 4-0-methyl-D-glucuronic acid was detected. The presence of this component was ascertained through methoxyl determination of 4-0-methylglucuronoxylan. This gave a value of 17.5 percent for the uronic acid residue in the acetylated "xylan." On the basis of these data the 0-acetyl-4-0-methylglucuronoxylan component contains an average of one uronic acid for each seven D-xylose units and about half of the D-xylose units contain an acetyl group. The glucomannan on hydrolysis provided D-glucose and D-mannose in the ratio of 1:1.

The composition of inorganic materials found in the original wood as the ash content and composition of these materials in the isolated cell wall polysaccharides as impurities were analyzed as a part of this study. This analysis was carried out with flame photometry for calcium, potassium, and sodium. Iron and phosphorus were determined by colorimetry following wet digestion. The data are presented in table 1 and this information is used for determining the effect of inorganic materials on thermal decomposition of wood and the effect on related cell wall polysaccharides. This information will also allow comparison with other thermal analyses reported in the literature.

⁶Includes acid decomposition products.

THERMAL ANALYSIS

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are commonly used to assess the thermal behavior of materials. The rate at which a material volatilizes as the temperature is raised in a controlled environment is shown by dynamic TGA. A small sample (usually <1 g.) is placed in the pan of an electronic balance suspended in a heated tube. As the system is heated, the weight loss of the sample is continuously recorded against temperature. In DTA a small sample and an inert reference material are heated in a silver block. As the heating continues at a constant rate, the sample undergoes various exo- or endothermic reactions or phase changes, which are detected in comparison with the inert material. The combination of DTA and TGA in conjunction with chemical methods provides a tool for detecting the nature of the pyrolytic reactions.

The thermal analysis curves can be analyzed through the following characteristics:

1. The initiation temperature, (T_i), or the onset of pyrolysis, as indicated by the beginning of weight loss on TGA, and/or the appearance of a peak on DTA;
2. The rate of weight loss, (R), shown by the slope of the TGA curve;
3. The residue (char), (C_T), remaining at a given temperature, (T), but normally after the period of rapid pyrolysis;
4. The temperature at which the peaks representing the endo- or exothermic reactions occur and the relative value of the enthalpy indicated by the area under the peak.

Thermal analysis is used for detecting the chemical kinetics and the energy of activation of the pyrolysis process. This would be valid if it is assumed that pyrolysis is a single reaction. However, nothing could be further from the truth. What actually is measured is the rate of weight loss caused by evaporation of numerous pyrolysis products.

Despite the fact that the data from thermal analysis describe the net effect, the characteristics which are tabulated above could be used for describing the general pyrolysis behavior of the substituents. The main objective of this analysis is to point out these characteristics and indicate how they are related to the thermal behavior of the original material.

Tang and others (Tang and Eickner 1968; Shafizadeh 1968) have found that the flame retardants generally decrease the rate of pyrolysis, R , in a dynamic environment, lower the initiation temperature, T_i , and increase the char, C_T .

Recently, Philpot has shown that the amount of silica-free minerals (SFA) in plant material could be correlated with the pyrolysis characteristics. A direct log-log relationship was found between SFA and maximum pyrolysis rate. The temperature at which the characteristic cellulose endotherm appeared showed a high correlation ($R^2 = 0.91$) with the SFA of the plant material. The char remaining at 400° C. could also be correlated with mineral content. There was some indication that the effect of the inorganic materials on the course of the pyrolytic reaction could vary according to the composition of the minerals.

The following procedures were used for obtaining the thermal analysis data. The thermal properties of cottonwood and its components were investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). These data were obtained

with a DuPont Model 900-950 thermal analyzer, programed at the rate of 15°/minute. The experiments were conducted in a nitrogen atmosphere, using silica beads as the reference for DTA and 5 or 10 mg. of the groundwood or its components as the sample. For TGA the gas flow was regulated at the rate of 100 ml./minute. Because Klason lignin is condensed and altered under the drastic acid treatment, it was augmented with milled wood lignin which is much closer to the native material (Browning 1963). The results obtained are shown in figures 2 and 3.

Figure 2.--Differential thermal analysis of cottonwood, cellulose, xylan, and lignin.

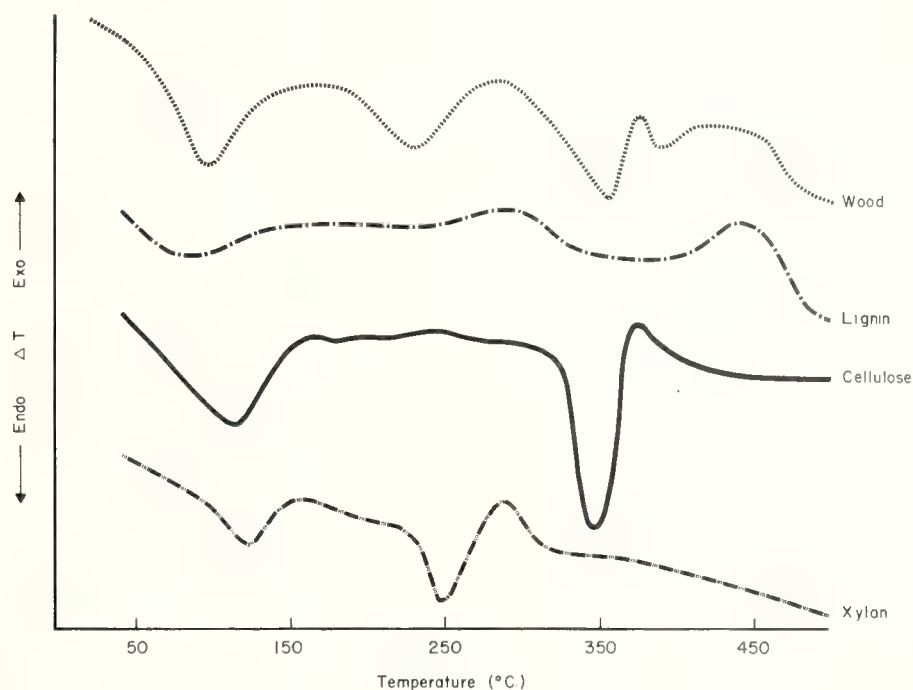
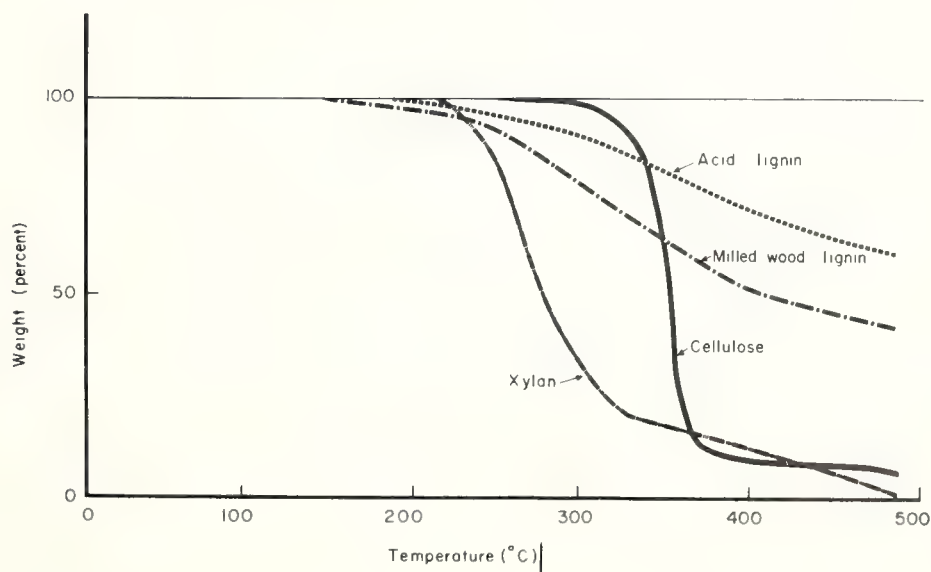


Figure 3.--Thermo-gravimetric analysis of cottonwood, cellulose, xylan, and lignin.



A summary of the thermal characteristics of cottonwood and its components are presented in table 2. These data indicate that the thermograms of cottonwood reflect the thermal behavior of its major components and the information that is obtained on these chemicals could be extrapolated to the original material with confidence. These data also show that under the experimental conditions (uncatalyzed reactions) lignin is the major source of char, but the carbohydrates are the precursor of the volatile products (tar and gases).

Table 2.--*The pyrolysis characteristics of cottonwood components*

Component	Temperature of initiation (T _i)	Maximum rate of pyro (R)	Residue at 450° C.
	°C.	mg./°C.	Percent
Wood	175	(¹)	19
Cellulose	320	.25	6
Xylan (DMSO)	215	.11	6
Milled wood lignin	175	.03	45
Acid lignin	200	.02	60

¹Wood exhibits two definite rates, one during xylan pyrolysis, the other during cellulose pyrolysis.

The most significant point about these data is the importance it places upon the pyrolysis of hemicellulose. Beall⁷ touched on this when he concluded, "The hemicelluloses appear to be the most important component in determining the rates of degradation of both softwoods and hardwoods." In addition to this we can see that xylan pyrolyzes almost completely prior to the beginning of pyrolysis of cellulose. Cellulose has been studied quite extensively in terms of ignition and other phenomena. It is quite clear that the hemicelluloses are of at least equal importance and may even provide the initial volatiles for ignition and combustion.

PYROLYSIS OF COTTONWOOD CELLULOSE

In this part of the current study the pyrolysis products from cellulose and the changes due to treatment with ZnCl₂ and NaOH were qualitatively and quantitatively determined under identical conditions in order to: (1) determine the effects of an acidic and an alkali additive on the composition of the volatile products and the pyrolytic reactions; (2) gain basic information about the mechanisms of the reactions involved by comparing these data with similar data from levoglucosan; and (3) extend the information that has been obtained from wood in which cellulose forms the major chemical component. Levoglucosan, 1,6-anhydro-β-D-glucopyranose, is currently being studied as a model compound for the secondary pyrolysis reactions of cellulose.

Treatment of cellulose consisted of adding 5 percent by weight of anhydrous zinc chloride or sodium hydroxide to a powdered sample. A small quantity of tetrahydrofuran was added to help evenly distribute the treatment. The treated material was then dried and stored under vacuum. The treatment procedure for both DMSO and base xylan was similar except it was found that about four-fifths of the sodium hydroxide was neutralized, probably by the glucuronic acid component. Therefore, 9 percent sodium hydroxide was used for alkali treatment of xylan.

⁷F. C. Beall. Thermal degradation analysis of wood and wood components. 1968. (Unpublished Ph.D. Thesis on file at Syracuse Univ., N.Y.)

Before investigating the effect of additives, it was desirable to determine the effect of the ash or natural inorganics on the pyrolysis of cellulose. Broido (1966) has pointed out that a contamination as little as 0.1 percent can significantly change the TGA of cellulose. Shown in figure 4 is a comparison of: commercially purified cellulose, ash content 0.01 percent;⁸ cotton cellulose, ash content 0.08 percent; and cottonwood cellulose, ash content 0.15 percent. This TGA shows cottonwood cellulose to behave differently than the "ash free" product and to behave similarly to the cotton cellulose with 0.08 percent ash.

As cellulose is heated from ambient to 500° C., the TGA and DTA curves clearly show the net effects. Cellulose had a maximum pyrolysis rate of 0.25 mg./°C. and a residue of 6 percent at 450° C. shown by TGA (fig. 5). The temperature of the beginning of active pyrolysis was 320° C. shown by TGA (fig. 5). The first endotherm corresponds to water loss and the second endotherm corresponds to major weight loss of the sample. A small exotherm is apparent subsequent to the second endotherm; it occurs at the secession of rapid weight loss.

The effects of ZnCl_2 on cellulose shown by TGA and DTA are to reduce the pyrolysis rate, lower the initiation temperature, and increase the residue. On the DTA curve (fig. 5), the major endotherm was somewhat reduced in size and the peak temperature was lowered drastically.

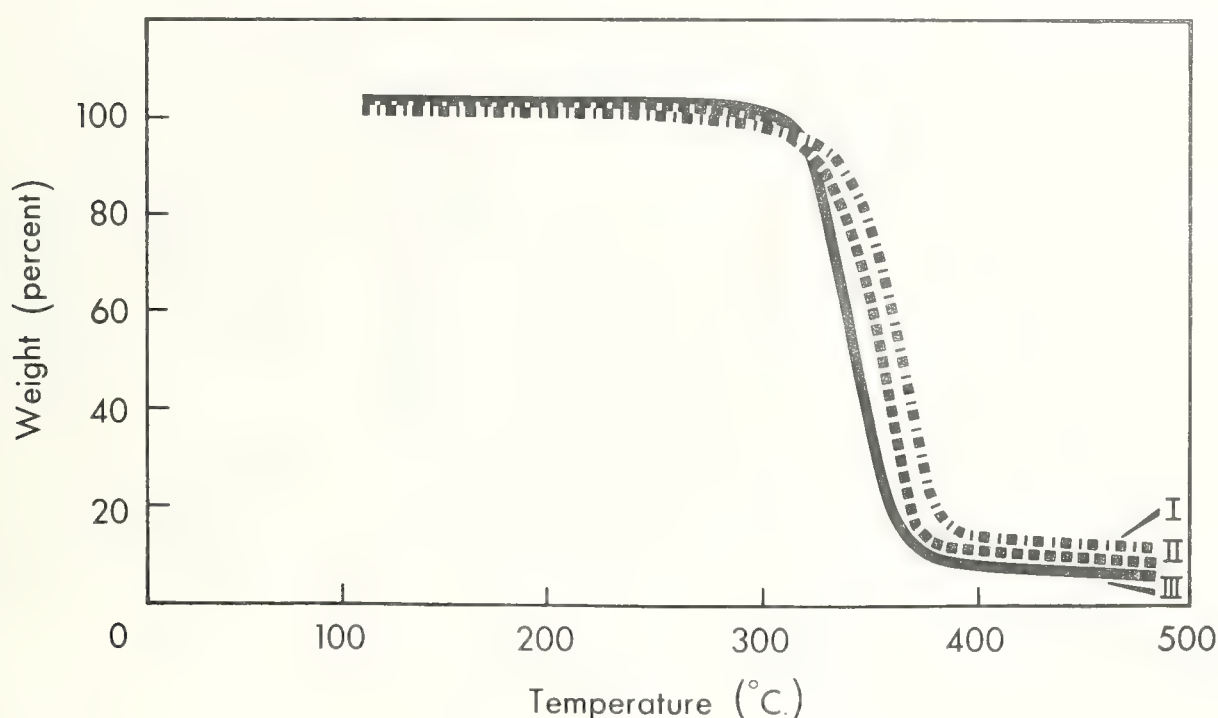


Figure 4.--Thermogravimetric analysis of: cotton cellulose, ash content 0.08 percent (I); cottonwood cellulose, ash content 0.15 percent (II); and commercial "ashless" cellulose, ash content 0.01 percent (III).

⁸Analytical filter pulp manufactured by Carl Schleicher and Schuell Co.

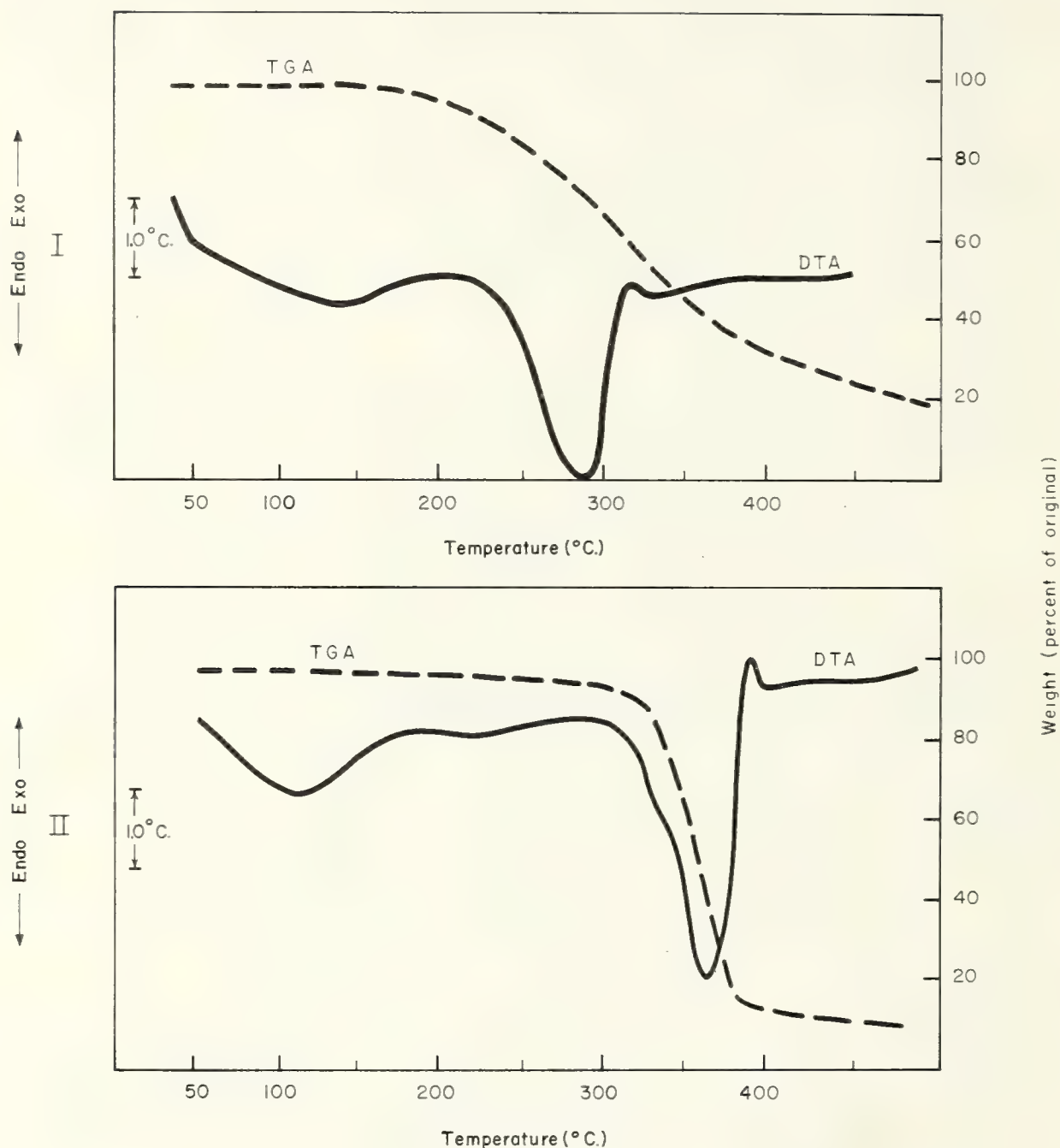


Figure 5.--Thermograms of cellulose (II) and cellulose treated with 5 percent zinc chloride.

The changes caused by NaOH are dissimilar to those caused by ZnCl_2 . The TGA shows the rate of weight loss to be slower for alkali treatment and the residue to be greater (fig. 6). On DTA an apparent exotherm, beginning at 175°C ., occurred, which was followed by a much reduced endotherm as compared to untreated cellulose. A large exotherm occurs from 275° to 350°C . and is the major difference between the two treatments. This is in agreement with the results of Mack and Donaldson (1967) for base treated cellulose. Table 3 lists the thermal properties of treated and untreated cellulose.

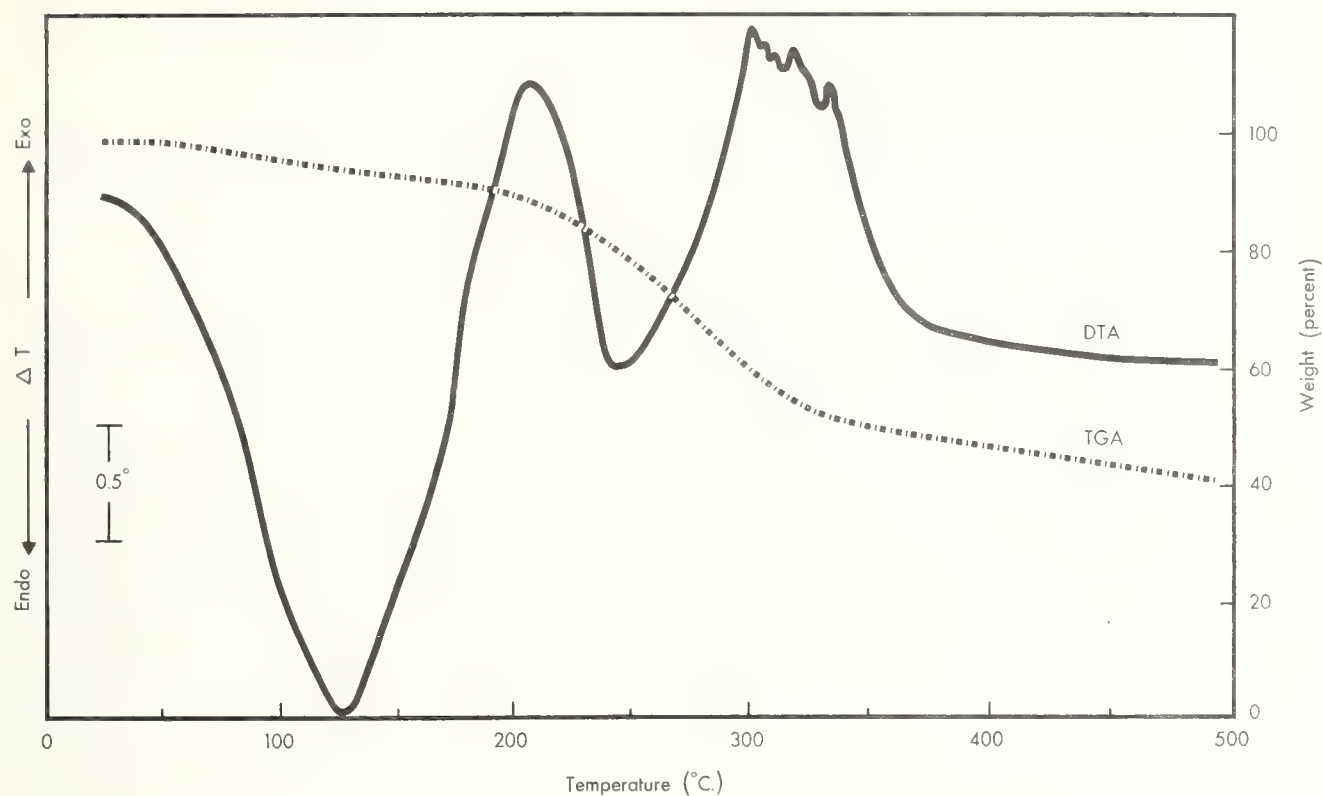


Figure 6.--Thermogram of cellulose treated with 5 percent sodium hydroxide.

Table 3.--Some thermal properties of cellulose and cellulose treated with 5 percent ZnCl_2 or 5 percent NaOH

Component	Maximum rate	Temperature of initiation (T_i)	Residue at 450° C.
	mg./°C.	°C.	Percent
Cellulose	0.25	320	6
Cellulose + 5 percent ZnCl_2	.05	220	38
Cellulose + 5 percent NaOH	.04	227	40

¹Organic basis.

The pyrolysis products from cottonwood cellulose and xylan, with and without treatment, were identified using pyrolysis GLC. To analyze the volatiles, about 12 to 20 mg. of the powdered samples were placed in a small aluminum boat and pyrolyzed at 600° C. in a Perkin Elmer pyrolysis unit connected to a Hewlett Packard F and M Model 5750 temperature programmed, dual column GLC.

The connections were modified to allow the carrier gas to either bypass the pyrolysis unit or sweep the pyrolysis products directly into the GLC unit. The volatile pyrolysis products were resolved by using essentially the previously reported conditions with minor modifications (Schwenker and Beck 1963).

The columns consisted of 12 feet of 1/4-inch diameter stainless steel packed with Fluoropak 80, coated with 10 percent of 20M carbowax. The carrier gas was helium flowing at the rate of 45 ml./minute for the thermal conductivity measurements and nitrogen flowing at the rate of 60 ml./minute for flame ionization. The column temperature was programmed between 50° and 210° C. at the rate of 2° to 8° C./minute. The flame ionization detector was sufficiently sensitive so that a 20:1 splitter could be used for collecting a major portion of the individual peaks for chemical identifications. The following methods were used for this purpose: (1) comparison of R_f values and spiking with known compounds; (2) mass spectroscopy of the side stream collected in a capillary tube cooled with liquid nitrogen; (3) u.v. spectroscopy of the collected material; (4) bubbling of the side stream in a solution 2,4-dinitrophenylhydrazine (DNPH) to form derivatives; (5) thin-layer chromatography (TLC) of the DNPH compounds (Byrne, Gardiner, and Holmes 1966); (6) m.p. of the DNPH derivatives; (7) i.r. spectrum of these materials; (8) Schiff's color test for aldehydes; (9) oxidation of an alcohol with KMnO_4 and TLC of the DNPH derivative of the resulting aldehyde; and (10) pH test for acids.

The GLC detectors were directly connected to a recorder and a Varian model 475 digital integrator. The integrator was calibrated by injecting known quantities of each compound. Carbon dioxide was identified by the precipitation of BaCO_3 from a $\text{Ba}(\text{OH})_2$ solution and quantitatively analyzed by titration with oxalic acid. Water was quantitatively analyzed with GLC using the thermal conductivity detector. The charred residue left after 20 minutes at 600° C. was weighed in the original aluminum boats.

A general consideration of the items listed in table 4 indicates two types of products. One results from the fragmentation of the glucose units such as acetaldehyde, glyoxal, 1-hydroxy-2-propanone, and acrolein. The other is the type of material that can be formed from the dehydration reactions such as water, char, and furan compounds. Both of these reactions probably operate in untreated cellulose, although the degradation apparently dominates, especially at the elevated temperatures. The effect of ZnCl_2 treatment was to increase the amount of furan compounds, water, and char. The NaOH treatment increased the 2 and 3 carbon carbonyl compounds as well as the char (figs. 7 and 8).

Table 4.--Pyrolysis products from cellulose (percent of original organic)

Peak No.	Compound	Cellulose	Cellulose +ZnCl ₂	Cellulose +NaOH	I.O. ident. method ¹
- - - - - Counts per mg. ² - - - - -					
1,2	Fixed gas	12,900	12,000	31,900	
- - - - - Percent - - - - -					
3	Acetaldehyde	1.3	1.0	3.1	1,5,6,7,8
4	Acetone/propionaldehyde	T ³	.2	T	1,5
5	Furan	1.4	3.2	.8	1
6	Acrolein	1.5	T	3.1	1,9
7	Methanol	.8	.5	.6	1,5,6,9
8	Methyl furan	T	2.1	T	1
10	2,3-Butanedione	1.4	1.2	2.4	1,4,5,8
11	2-Butenal	.8	2.1	1.9	1,4,5,6,8
13	2-Oxypropanal	T	.8	T	1,5
15	1-Hydroxy-2-propanone	1.9	.3	1.4	1,5
16	Glyoxal	2.0	.1	6.9	1,5,6
17	Acetic acid	.8	.8	3.5	1,2,10
18	2-Furaldehyde	.9	2.1	1.0	1,2,3,4,5,6
19	Formic acid	T	T	1.7	1,10
20	5-Methyl-2-furaldehyde	.3	.3	.3	1,5
21	Furfuryl alcohol	.3	.3	.1	1
	H ₂ O	11	16	12	
	CO ₂	6	4	8	
	Char	5	23	18	

¹Refer to methods on page 12.²Counts per mg. at attenuation 10³-16.³T = <0.1 percent

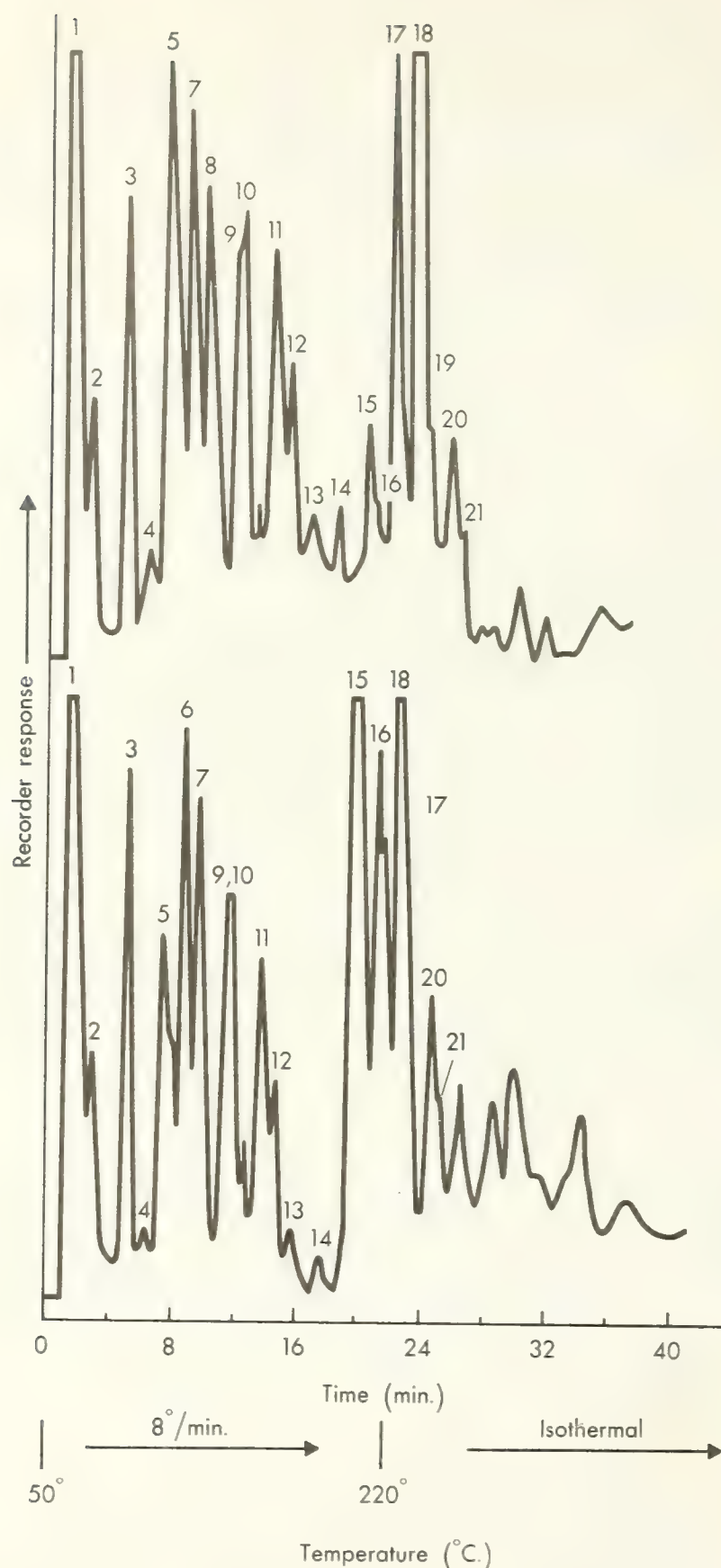


Figure 7.--Chromatogram of the pyrolysis products of cellulose (lower) and cellulose treated with 5 percent zinc chloride. The peaks are (1), (2) fixed gases; (3) acetaldehyde; (4) acetone/propionaldehyde; (5) furan; (6) acrolein; (7) methanol; (8) methyl furan; (10) 2,3-butanedione; (11) 2-oxypropanal; (15) 1-hydroxy-2-propanone; (16) glyoxal; (17) acetic acid; (18) 2-furaldehyde; (19) formic acid; (20) 5-methyl-2-furaldehyde; and (21) furfuryl alcohol.

PHILPOT, CHARLES W.

1971. The pyrolysis products and thermal characteristics of cottonwood and its components, USDA Forest Serv. Res. Pap. INT-107, 31 p., illus.

This study was undertaken to determine the thermal properties of, and the pyrolysis products from, western cottonwood (*Populus trichocarpa*) and two of its major components: cellulose and xylan. The modifications due to treatment of the wood and its components with an acid and alkali were also documented. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA), as well as direct pyrolysis into a temperature-programmed gas-liquid chromatograph, were used in this investigation.

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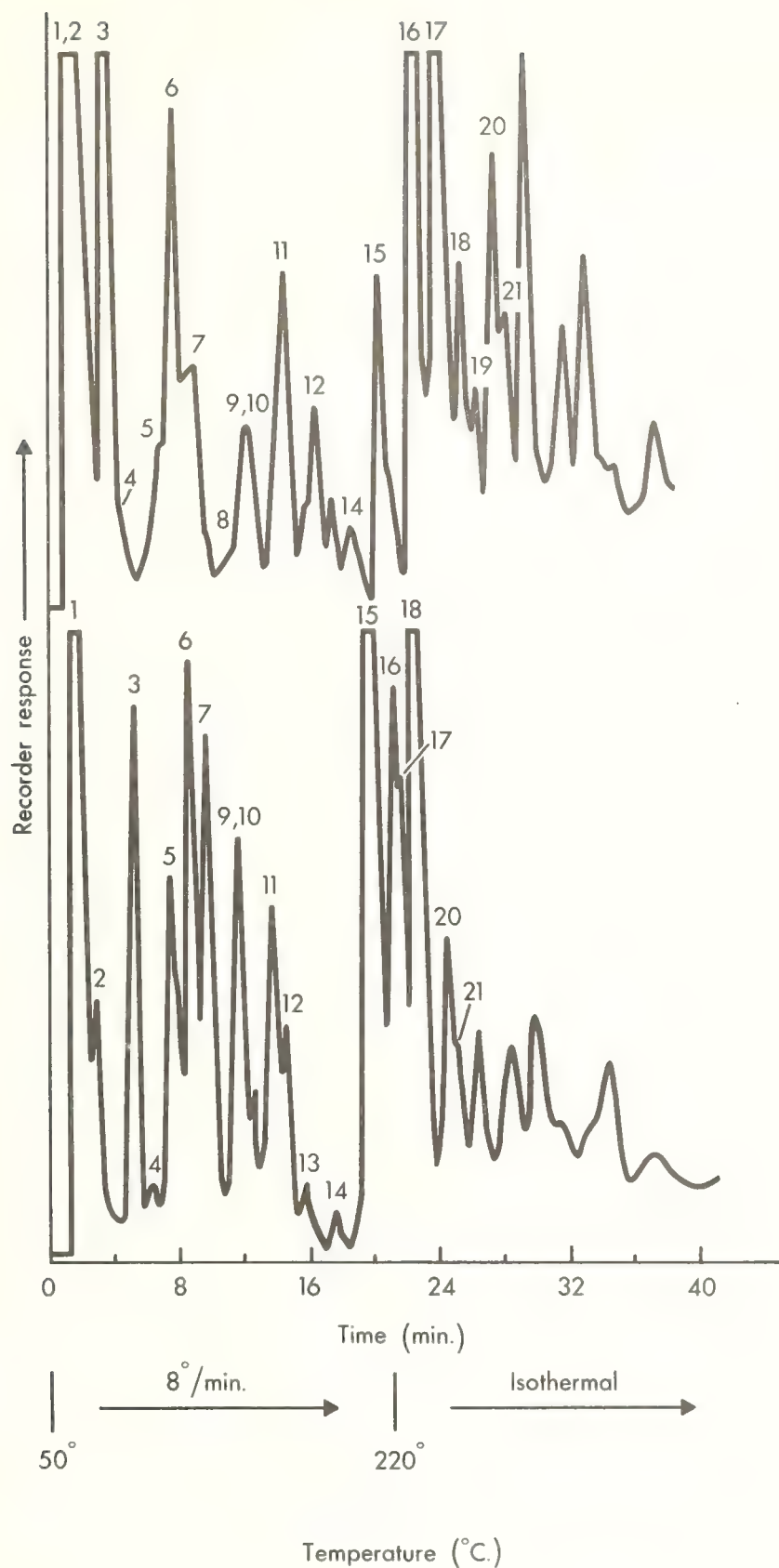


Figure 8.--Chromatogram of cellulose treated with 5 percent sodium hydroxide (see figure 7 for identification of peaks).

PYROLYSIS OF XYLAN

The hemicellulose fraction of cottonwood is mainly 0-acetyl-4-0-methylglucuronoxylan (i.e., xylan). The isolation of the polysaccharide was described in a previous section. The pyrolysis studies in the past have mainly dealt with cellulose and there is little thermal degradation data on xylan. Beall⁹ has reported a thermal analysis study (TGA and DTA) of hemicelluloses from different species of wood, without inorganic chemical analysis of samples. The early investigation of the products formed from xylan pyrolysis has been limited to identification of a few major compounds, especially furfural (2-furaldehyde) (Heuser and Scherer 1923).

A recent report deals with the thermal analysis of xylan isolated from beechwood, and includes a complete chemical analysis of the substrate (Shimizu, Teratani, and Miyazaki 1968). This study showed that pyrolysis of xylan takes place at about 215° C. when the polysaccharide structure disappears, as shown by IR spectroscopy. When xylan was heated further to 290° C., fragmentation of the compound occurred. Shimizu and co-workers also claimed that some polymerization, evidenced by the appearance of xylobiose above 275° C., could take place. The fragmentation and polymerization gave a net exothermic reaction which was not resolved. Maximum weight loss occurred between 215° and 290° C.

Further studies by McGinnis¹⁰ have shown that the initial pyrolytic reaction involves breaking of the β 1 \rightarrow 4 glycosidic bond through a carbonium ion mechanism. This conclusion is mainly based on investigation of methyl, and substituted phenyl β -D-xylosides, used as model compounds for xylan. The nature of the aglycone for these xylosides provided a wide range of glycosidic bonds. By subjecting the models to DTA and TGA, it was shown that the thermal stability of the glycosidic bonds was determined by the electron withdrawing power of the aglycone. Analysis of the products showed that the aglycone could be recovered quantitatively and therefore the 1 \rightarrow 4 glycosidic bond must have been broken during the initial stage of the reaction.

Two kinds of xylan were described previously: the DMSO-extracted xylan which remains acetylated as in the native form, and the base-extracted xylan which has been deacetylated by the alkali. In this part of the program, both types of treated and untreated xylan were subjected to DTA and TGA as well as pyrolysis gas chromatography.

Thermal analysis of both types of xylan showed very little difference between them. The TGA (fig. 9) shows that pyrolysis began at 215° C. as indicated by weight loss and proceeded rapidly up to 275° C. The maximum rate of pyrolysis was 0.11 mg./°C. and a residue of 6 percent remained at 450° C. (table 5).

In the DTA curve there was an endotherm at the onset of rapid weight loss. This was followed by a sharp exotherm (fig. 10). Figures 9 and 10 show the effects of 5 percent ZnCl₂ on the TGA and DTA of base-extracted xylan. On TGA, weight loss began at 175° C. as compared to 215° C. for the untreated. The maximum rate of weight loss was 0.06 mg./°C. and a residue of 2 to 5 percent remained at 450° C. On DTA, the endotherm corresponding with rapid weight loss occurred from 175° to 225° C. and was followed by a broad exothermic region (fig. 10).

⁹ Beall, op. cit.

¹⁰ McGinnis, op. cit.

Table 5.--Some thermal characteristics of DMSO and base xylan treated with 5 percent ZnCl_2 and 9 percent NaOH

Component	Maximum rate (R)	T_i	Residue ¹
	mg./°C.	°C.	Percent 450° C.
Base xylan	0.11	215	6
DMSO xylan	.11	215	6
Base xylan + 5 percent ZnCl_2	.06	175	25
DMSO xylan + 5 percent ZnCl_2	.06	175	25
Base xylan + 9 percent NaOH	.07	200	27
DMSO xylan + 9 percent NaOH	.06	200	31

¹Organic base.

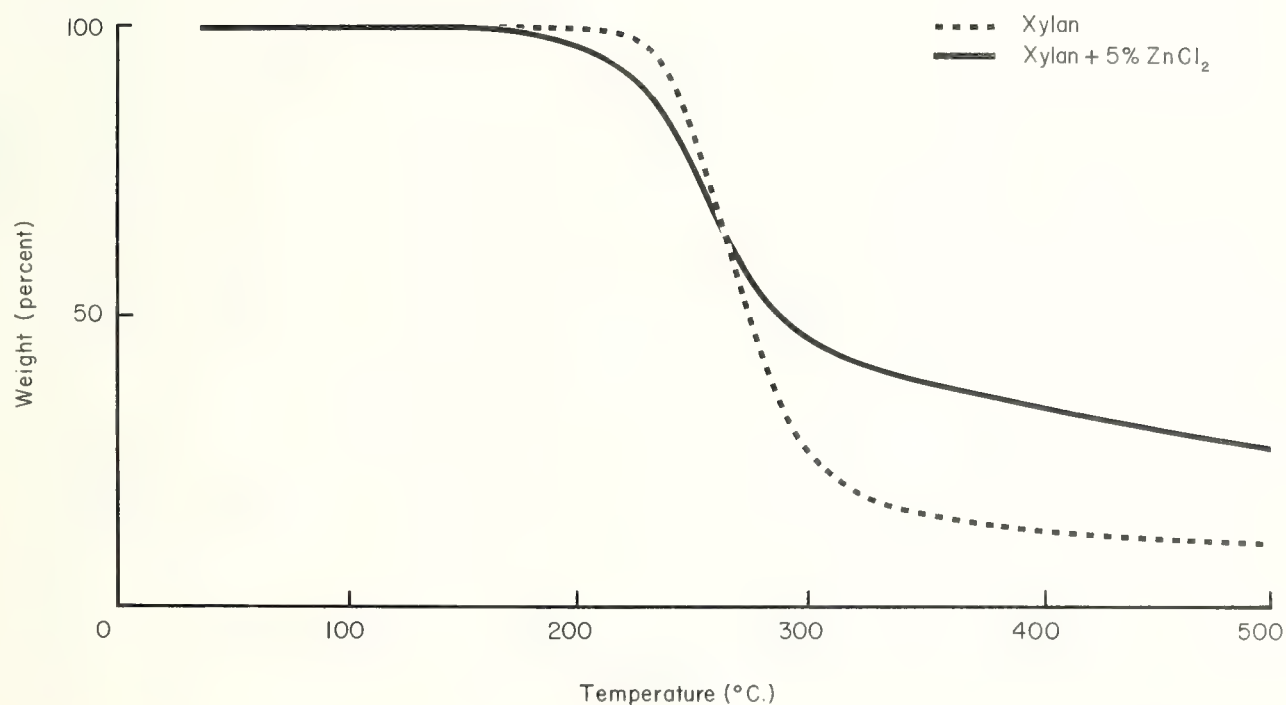


Figure 9.--Thermogravimetric analysis of DMSO xylan and DMSO xylan treated with 5 percent zinc chloride.

Figure 10.--Differential thermal analysis of DMSO xylan and DMSO xylan treated with 5 percent zinc chloride.

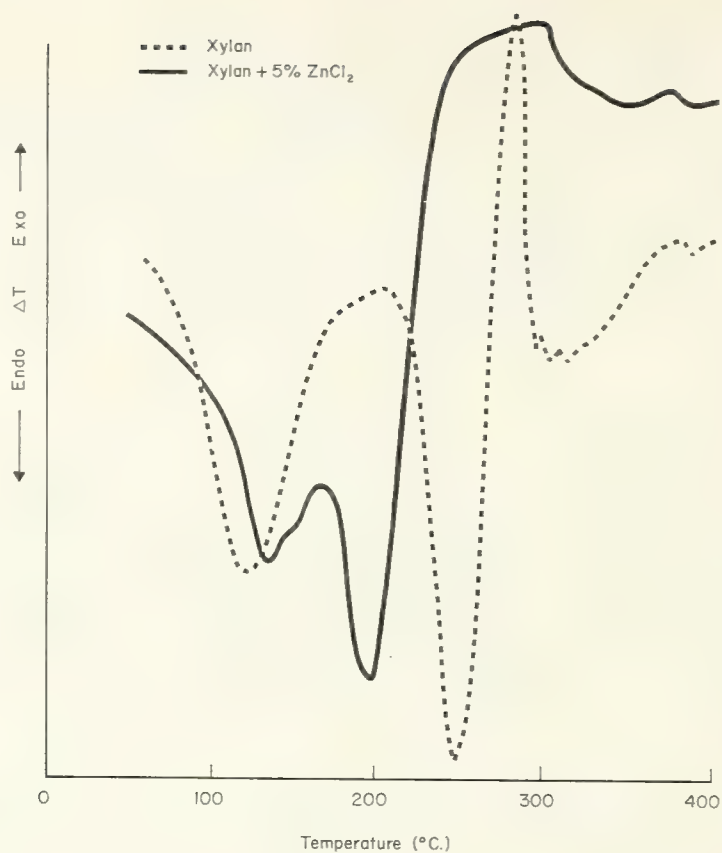


Figure 11.--Thermogravimetric analysis of DMSO xylan (II), and base xylan (I), treated with 9 percent sodium hydroxide.

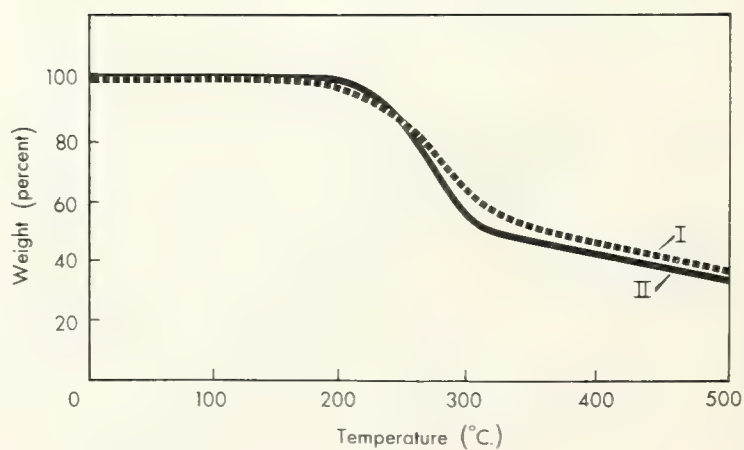


Figure 12.--Differential thermal analysis of DMSO xylan treated with 9 percent sodium hydroxide.

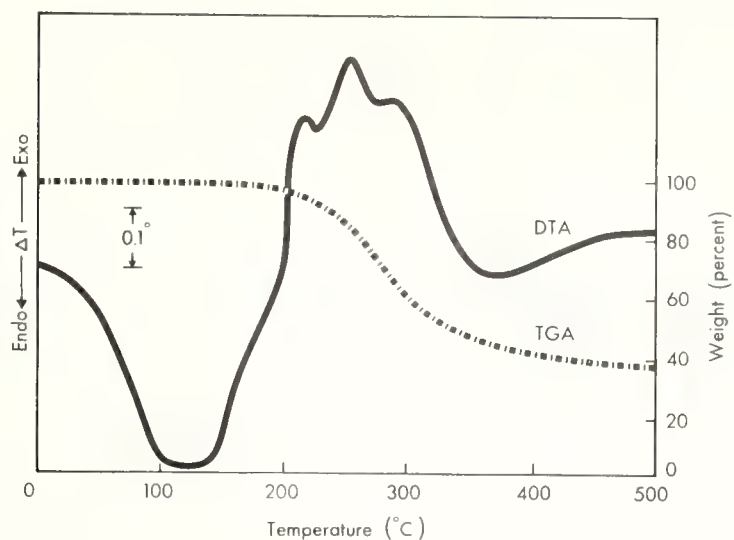
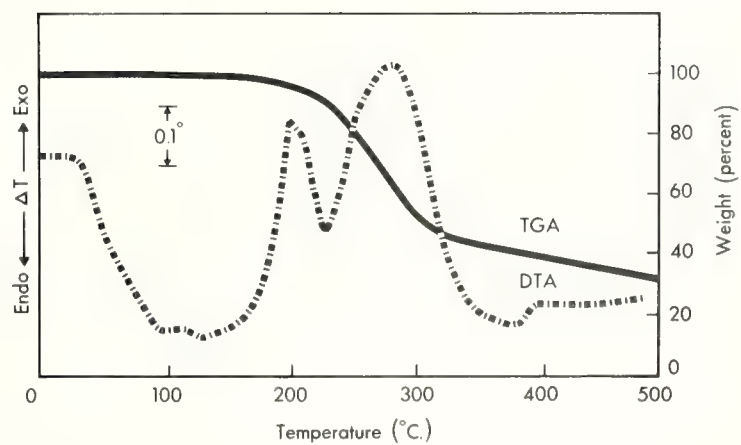


Figure 13.--Differential thermal analysis of base xylan treated with 9 percent sodium hydroxide.



The untreated DMSO- and base-extracted xylans behaved quite similarly in a thermal environment; however, the two types of xylan showed major differences when treated with alkali. Thermal analysis and pyrolysis gas chromatography showed that xylan treated at the 5 percent level of NaOH was quite similar to that which was untreated. Apparently the glucuronic acid component of the xylan neutralized about 4/5 of the alkali so the treatment was increased from 5 to 9 percent. The TGA of DMSO- and base-extracted xylan treated with 9 percent NaOH is shown in figure 11. The DMSO-extracted xylan had a higher residue and a slower rate of pyrolysis. This may be due to the greater neutralizing effect of the base-extracted xylan because there are more glucuronic acid units present per unit weight.

Figure 12 shows the TGA and DTA of DMSO-extracted xylan treated with 9 percent NaOH. The onset of rapid weight loss on TGA showed active pyrolysis to begin at 200° C. The maximum rate of pyrolysis was 0.06 mg./°C. and the residue at 450° C. was 31 percent. There was a net exotherm from 200° to 325° C. during rapid weight loss shown on DTA (fig. 12). The DTA of base-extracted xylan treated with 9 percent NaOH showed an endotherm at the onset of rapid weight loss and a subsequent exotherm from 225° to 325° C. (fig. 13). The maximum weight loss rate was 0.07 mg./°C. and the residue at 450° C. was 27 percent.

Neat DMSO- and base-extracted xylan were pyrolyzed and the products swept directly into the GLC. The major products were identified by the previously described methods (table 6, fig. 14). As expected, much more 2-furaldehyde was produced from xylan as compared to cellulose. The large amount of acetic acid from DMSO-extracted xylan was quantitatively equal to the acetate groups, plus what was produced from the deacetylated product. However, the DMSO-extracted xylan produced twice as much H₂O, half as much acetaldehyde and 2-furaldehyde, and some other differences that could not be readily explained.

The two types of xylan were treated with the additives so that the pyrolysis products could be identified, quantified, and compared to those of treated cellulose and wood. Treatment of both xylans with 5 percent ZnCl₂ had an effect similar to that found for treated cellulose (fig. 14). There was an increase in furan compounds and a decrease in 2 and 3 carbon carbonyl compounds (table 6). However, the acetaldehyde produced from the ZnCl₂ treated DMSO-extracted xylan was about twice that of the untreated DMSO-extracted xylan. The 2-furaldehyde was increased by 2.2 times for both types of xylan treated with 5 percent ZnCl₂, although there was still twice as much 2-furaldehyde produced from the base-extracted xylan.

The effects of 9 percent treatment on both types of xylans also produced results (table 6) generally similar to alkali-treated cellulose (fig. 15). The small carbonyl compounds increased and the furan compound decreased. The compounds showing the greatest increase were acetone, propionaldehyde, and crotonaldehyde. There was also an increase in CO₂ and H₂O.

Table 6.--Pyrolysis products from xylan (percent of organic original)

Peak no.	Compound	Neat		5% ZnCl ₂		9% N ₂ OH	
		DMSO	Base	DMSO	Base	DMSO	Base
----- Counts per mg. ¹ -----							
1,2	Fixed gases	18,100	20,400	5,500	5,000	19,400	14,800
----- Percent -----							
3	Acetaldehyde	1.0	2.4	1.9	.1	1.6	1.6
4	Furan	2.2	T ²	3.5	2.0	.4	.3
5	Acetone			T	T		3.3
		1.4	0.3			5.8	
6	Propionaldehyde			T	T		.7
7	Methanol	1.0	1.3	1.0	1.0	1.8	2.1
11	2,3-Butanedione	T	T	T	T	T	T
12	Ethanol	T	T	--	--	.6	.6
13	Crotonaldehyde	T	T	--	--	1.4	1.2
14	1-Hydroxy-2-propanone	.5	.4	T	T	.8	
							2.0
15	Acetoin	.6	.6	T	T	.6	
16	Acetic acid	10.3	1.5	9.3	T	3.4	3.1
17	2-Furaldehyde	2.2	4.5	5.0	10.4	.6	1.6
	Char	10	10	23	26	23	21
	CO ₂	8	8	6	7	22	14
	H ₂ O	14	7	15	21	19	26

¹Counts per mg. at attenuation 10³-32.²Less than 0.1 percent.

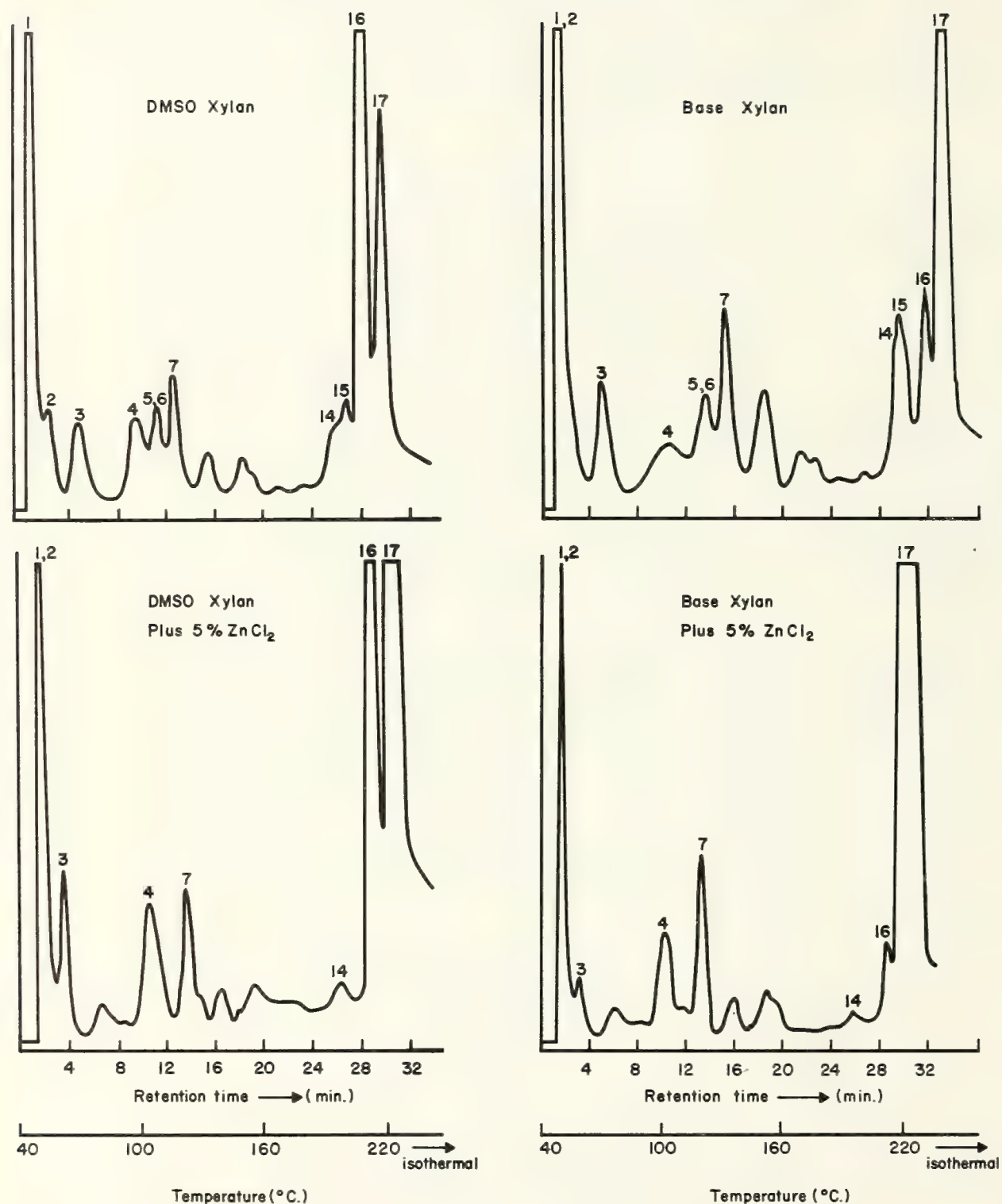


Figure 14.--Chromatograms of DMSO and base xylan with and without treatment with 5 per-cent zinc chloride. The peaks are: (1), (2) fixed gases; (3) acetaldehyde; (4) furan; (5) acetone; (6) propionaldehyde; (7) methanol; (11) 2,3-butanedione; (12) ethanol; (13) crotonaldehyde; (14) 1-hydroxy-2-propanone; (15) acrolein; (16) acetic acid; and (17) 2-furaldehyde.

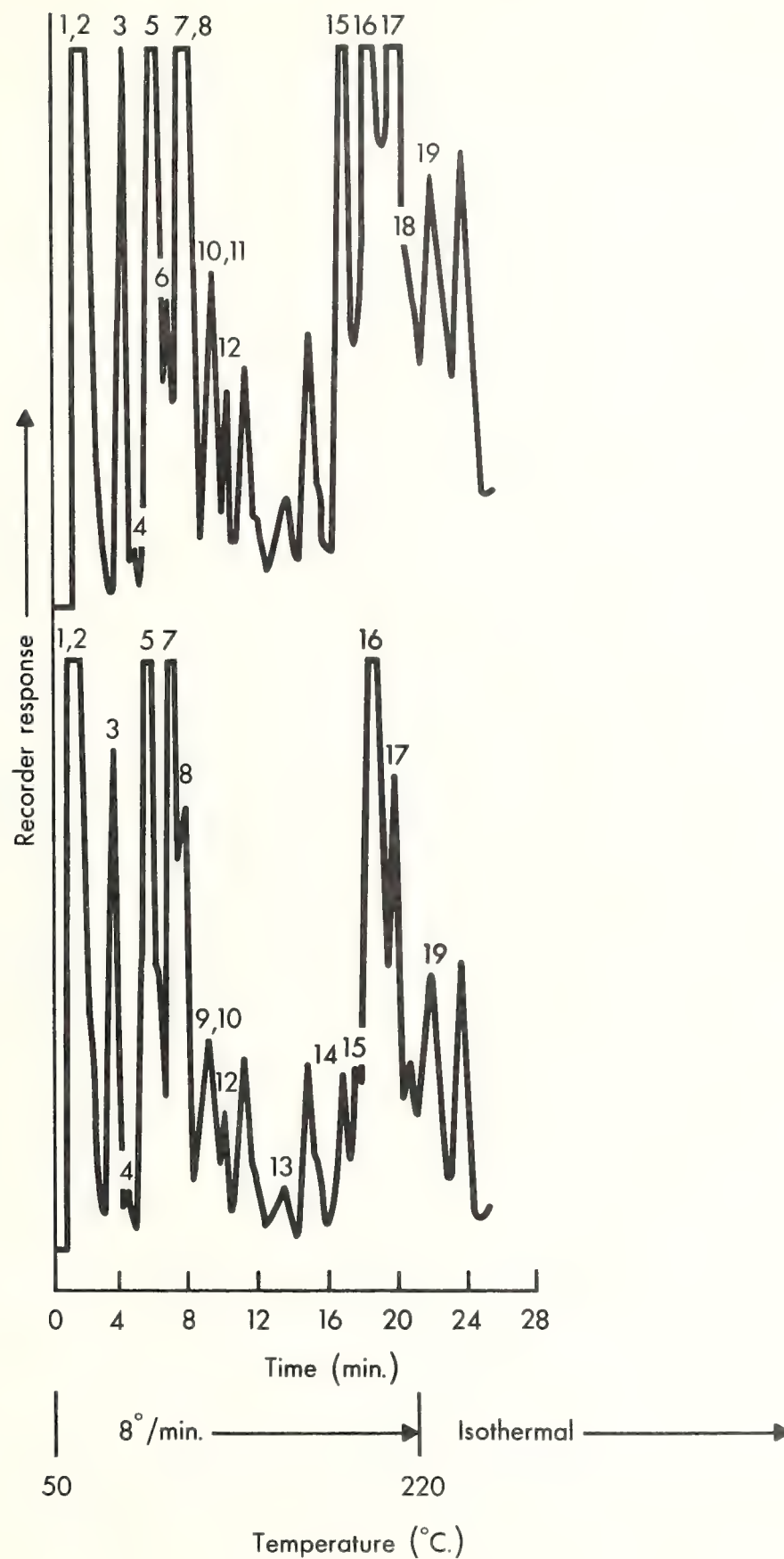


Figure 15.--Chromatograms of DMSO and base xylan treated with 9 percent sodium hydroxide (see figure 14 for peak identification).

PYROLYSIS OF COTTONWOOD

One of the goals of this study was to investigate the pyrolysis of whole wood and its major components with and without the presence of additives. In order to carry this out, cottonwood was studied by TGA, DTA, and pyrolysis GLC, using the methods previously described. The thermal analysis of untreated cottonwood was presented in a previous section. The pyrolysis products from untreated cottonwood, cottonwood treated with 5 percent ZnCl_2 , or 5 percent NaOH , as well as the TGA and DTA of treated wood, will be presented in this section. Since lignin complicates the study of wood, some work with this component was necessary. The TGA of lignin has been previously presented and a limited amount of pyrolysis GLC data is discussed here. As previously noted, the thermogram of cottonwood is quite complex. Pyrolysis of each component can be identified by its characteristic thermal behavior and the thermogram of the whole wood is a composite of the thermal behavior of all of the components.

Treatment of cottonwood with 5 percent ZnCl_2 , which can be observed by DTA (fig. 16), shows the effect of this additive on each component. The xylan endotherm beginning at 175°C . and the cellulose endotherm beginning at 240°C . were both present. However, the net endotherm from cellulose was greatly reduced by the exotherm of xylan from 250° to 300°C . The TGA also appears to be a composite of the pyrolysis behavior of the components. Table 7 shows computations which account for the char from TGA of wood and its components, assuming no effect of ZnCl_2 or NaOH on the amount of lignin char.

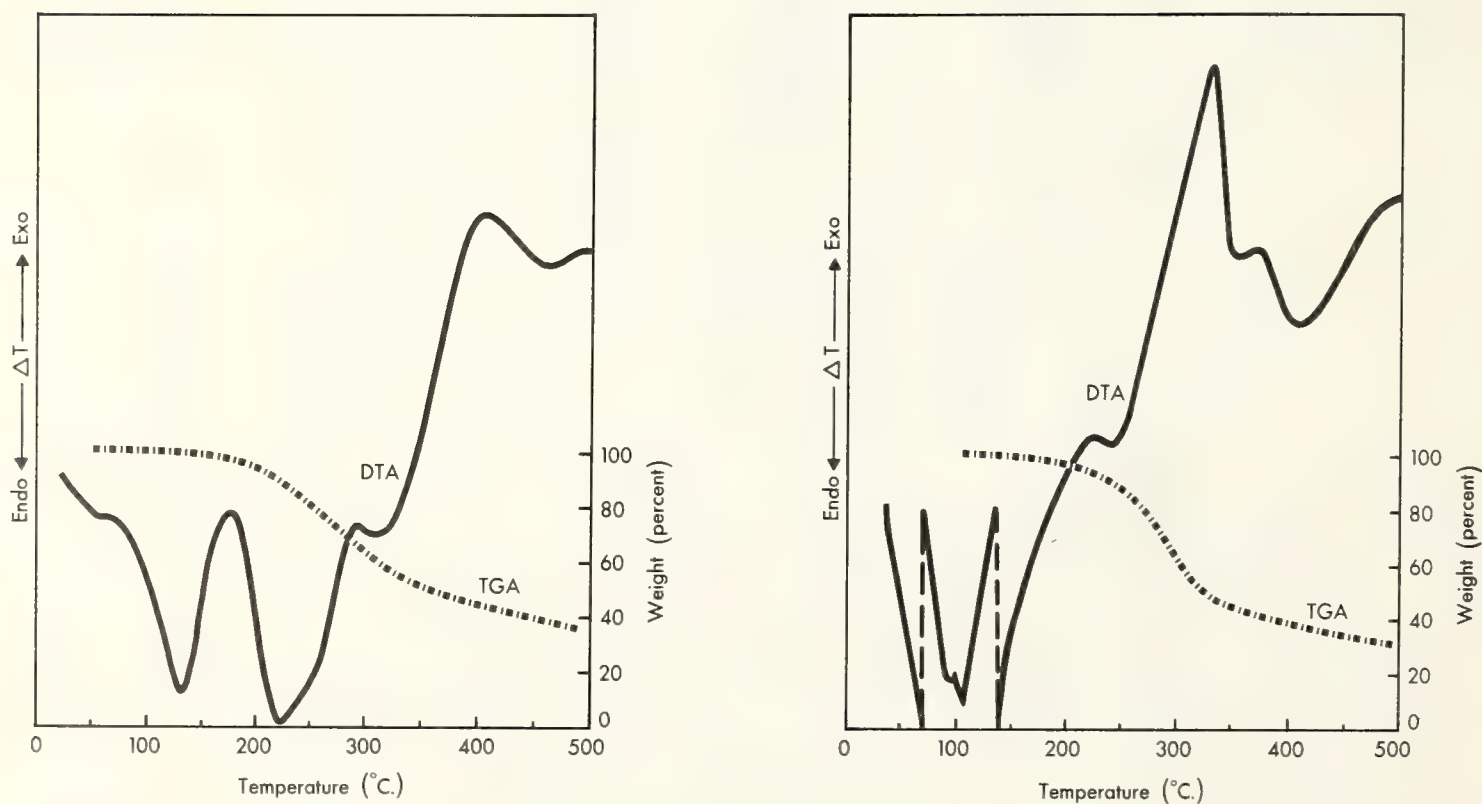


Figure 16.--(Left) Thermogram of cottonwood treated with 5 percent zinc chloride.
(Right) Thermogram of cottonwood treated with 5 percent sodium hydroxide.

Table 7.--Comparison of char from cottonwood and its components

Component	Composition percent	Char formed (percent)					
		Neat		ZnCl ₂		NaOH	
		A ¹	B ²	A	B	A	B
Cellulose	44	6	2.6	33	14.5	22	9.7
Xylan	21	6	1.3	27	5.7	31	6.5
Milled wood lignin	32	45	14.4	45	14.4	45	14.4
Sum of char from components		18.3		34.6		30.6	
Actual organic char from wood		19.0		35.0		30.0	
Difference		-.7		-.4		.6	
Error (percent)		3.7		1.1		3.2	

¹ Residue at 450° C. from TGA minus treatment in percent.

²Net char at 450° C. X percent the component makes up of whole wood.

The effects of 5 percent NaOH on the pyrolysis of cottonwood can be seen on DTA as being generally made up of the combined effect of alkali on cellulose and xylan. The net process was exothermic after water loss (fig. 16). A slight dip occurred in the DTA trace at about 240° C. and corresponds to the endotherm at that temperature on the DTA of cellulose treated with alkali (fig. 6). The TGA shows a char which was equal to the weighted chars from the alkali treated components (table 7).

The volatile products from the pyrolysis of wood were qualified and quantified using previously described methods. Milled wood lignin was studied by pyrolysis gas chromatography so that any major peaks from this component could be identified on the chromatogram of wood.

The pyrolysis of milled wood lignin gave four major peaks on the chromatogram (fig. 17). In addition to fixed gases, these peaks appeared to be methanol (L₁), acetic acid (L₂), and the largest peak, (L₃), which is unidentified. Kitao and Watanabe (1967) identified several products from the pyrolysis of beech milled wood lignin. Three major peaks, presumably of low molecular weight, were not identified in the paper, but they could certainly be methanol, ethanal, and acetic acid. The products they did identify formed relatively minor peaks except for a combined peak of transisoeugenol and pyrogallol-1, 3-dimethylether. Possibly this is the major peak labeled L₃ on the chromatograms, but, due to differences in columns and wood species, little can be said concerning the identity of the peak. It should be noted that the same peak, (L₃), appears in all the chromatograms of wood and is greatly reduced by ZnCl₂ treatment (figs. 17 and 18). The possibility of using this pyrolysis procedure to quantify lignin content should be investigated to see if this time-consuming procedure could be automated.

Figure 17.--(Upper) Chromatogram of cottonwood (see figure 7 for peak identification).
(Lower) Chromatogram of milled wood lignin (see text for description).

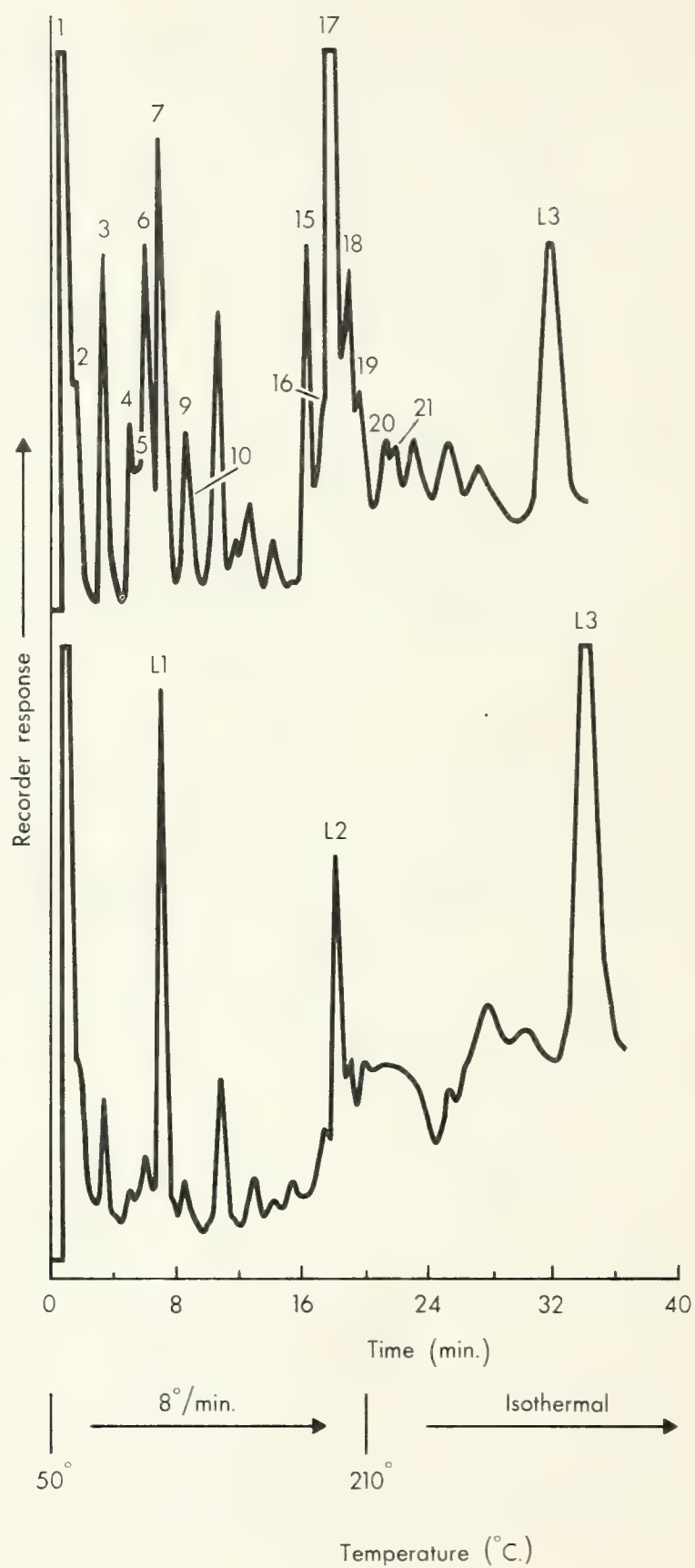
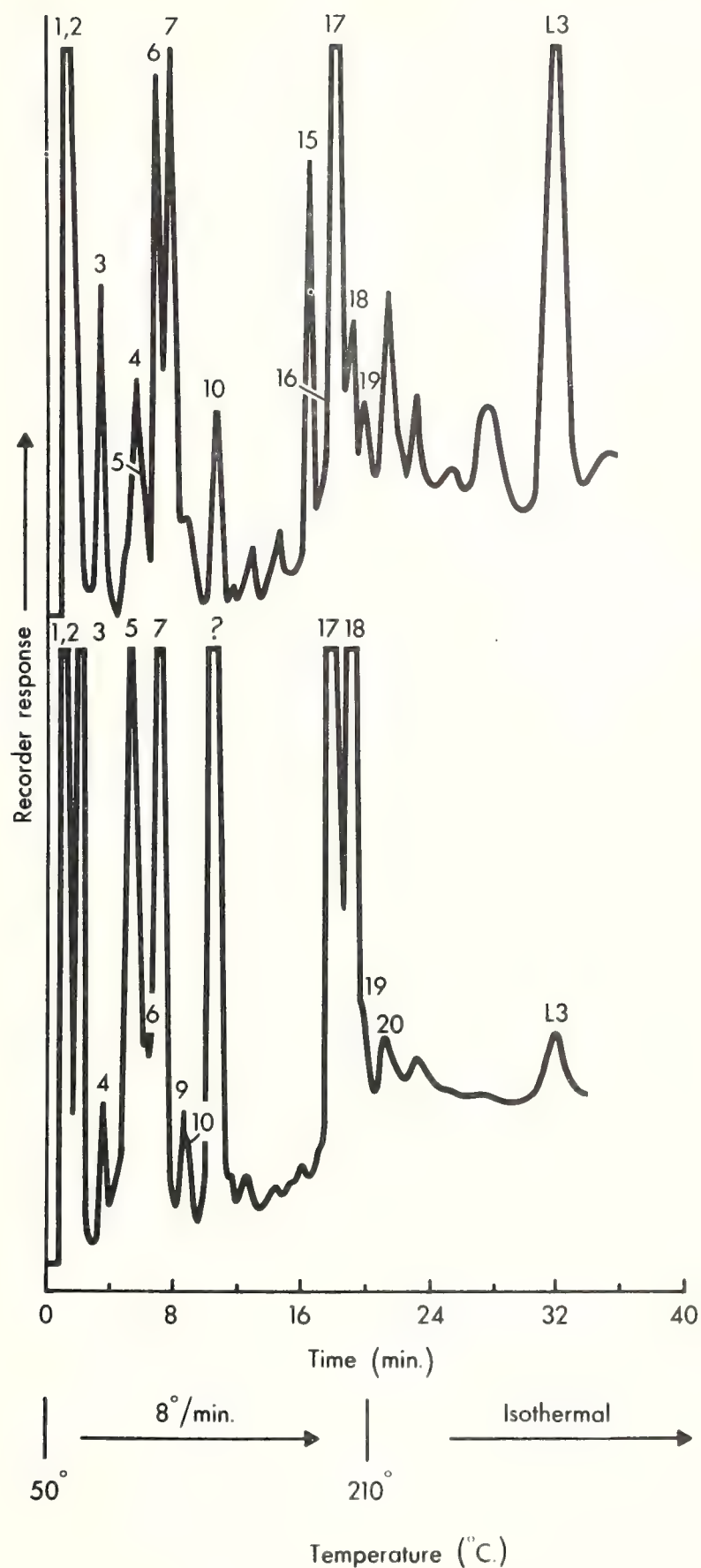


Figure 18.--Chromatogram of cottonwood treated with 5 percent sodium hydroxide (upper) and 5 percent zinc chloride (lower) (see figure 7 for peak identification).



The chromatogram from the pyrolysis of cottonwood is shown in figure 17. These products are quantified in table 8. Additional compounds identified for both cellulose and cottonwood were levulenic acid (retention time) and 5-(hydroxymethyl)-2-furaldehyde (retention time and TLC). All of the major peaks can be identified from the chromatograms of cellulose, xylan, and lignin.

The chromatogram of cottonwood treated with 5 percent ZnCl_2 is shown in figure 18. The products are quantified in table 8. Generally, the effect of ZnCl_2 was similar to that which occurred when the same treatment was given xylan and cellulose. With the exception of acetaldehyde, furan compounds increased and 2-3 carbon compounds decreased. The peak identified by a question mark in figure 18 was also greatly increased by the ZnCl_2 treatment; this peak was probably due to the effect of the treatment on lignin. Until lignin is more completely investigated, extrapolation of the volatiles produced from the components to the whole wood will be difficult.

Treatment of wood with 5 percent NaOH increased the production of 2 and 3 carbon fragments. This is similar to what occurred when cellulose and xylan were treated with alkali (fig. 18). However, there was no reduction in the amount of furan compounds produced from untreated wood.

Table 8.--Pyrolysis products from wood

Peak no.	Compound	Amount			
		Wood	+ZnCl ₂	+NaOH	I.D.
-----Counts per mg.-----					
1,2	Fixed gases	21,900	9,100	31,800	
-----Percent-----					
3	Acetaldehyde	2.3	4.4	3.4	1,5,6,7,8
4	Acetone/propionaldehyde	1.5	.9	3.2	1,5
5	Furan	1.6	7.9	1.7	1
6	Acrolein	3.2	.9	4.8	1,9
7	Methanol	2.1	2.7	5.7	1,5,6,9
8	Methyl furan	*1	*	*	1
10	2,3-Butanedione	2.0	1.0	5.6	1,4,5,8
15	1-Hydroxy-2-propanone	2.1	T ²	3.4	1,5
16	Glyoxal	2.2	T	1.5	1,5,6
17	Acetic acid	6.7	5.4	7.3	1,2,10
18	2-Furaldehyde	1.1	5.2	1.0	1,2,3,4,5,6
19	Formic acid	.9	.5	1.6	1,10
20	5-Methyl-2-furaldehyde	.7	.9	1.0	1,5
21	Furfuryl alcohol	.5	T	.8	1
	CO ₂	12.1	6.0	13.8	
	H ₂ O	18.0	18.4	20.1	
	Char	15.0	24.0	30.0	

¹ * = not clearly identifiable for wood.

² T = approximately 0.1 percent.

SUMMARY AND CONCLUSIONS

The major conclusions from this study are:

1. The major component of western cottonwood hemicellulose is 0-acetyl-4-0-methyl glucuronoxylan (xylan), making up about 95 percent of the noncellulose carbohydrate.

2. The three major components of western cottonwood, cellulose, xylan, and lignin have quite dissimilar thermograms, but all three are reflected in the thermogram of the whole wood. This independent behavior makes it quite likely that each component can be studied independently and the results used to predict its behavior within whole wood. This greatly simplifies the study of the complicated pyrolysis of wood.

3. The hemicellulose 0-acetyl-4-0-methyl glucuronoxylan is almost completely pyrolyzed prior to the beginning of cellulose pyrolysis. This makes the hemicellulose component more important to the fire problem than generally thought, especially since the pilot ignition temperature is around 300° to 340° C.

4. Lignin is the least important component in the pyrolysis of wood because of its products, rate of decomposition, and high yield of char. Since the char probably contributes mainly to glowing, lignin may be quite important to the hold-over fire in punk or decomposed plant material.

5. Contrary to past work (Schwenker and Beck 1963), no formaldehyde from the pyrolysis of these carbohydrates was found. This agrees with Wodley (1969).

6. Cellulose, xylan, and wood all exhibit dissimilar thermograms and volatile products between zinc chloride and sodium hydroxide treatment. The zinc chloride produces more of the furan compounds, especially 2-furaldehyde, and a decrease in 2 and 3 carbon compounds. The sodium hydroxide decreases the furan compound and increases 2 and 3 carbon compounds. Obviously these two model retardants are acting by dissimilar mechanisms.

7. Zinc chloride and sodium hydroxide both cause an increase in char and water production. This probably means they both lead to more glowing combustion than would occur with the untreated fuel. However, any flame retarding effect is due to a combination of decreases in volatilization amount and rate as well as increases in water and char production. Since these two compounds act differently, each effect must be weighted accordingly.

LITERATURE CITED

- Broido, A.
1965. Effects of fire on major ecosystems. Pp. 11-19, in Ecological effects of nuclear war. G. M. Woodwell, Editor. Upton, N.Y. Brookhaven Nat. Lab.
- _____, and S. B. Martin
1966. Thermogravimetric and differential thermal analysis of bicarbonate treated cellulose. *Pyrodynamics* 4: 243.
- _____, and S. B. Martin
1961. Effect of potassium bicarbonate on the ignition of cellulose by radiation. *Fire Res. Abstr. Rev.* 13(3): 193.
- Browning, B. L.
1963. The chemistry of wood. New York: Intersci. Publ.
- Butin, H.
1960. Germination of spores of *Dothichiza populae* in aqueous extracts of various poplar species. *Ber. Deut. Bot. Ges.* 73: 185.
- Byrne, G. A., D. Gardiner, and F. H. Holmes
1966. The pyrolysis of cellulose and the action of flame retardants. *J. Appl. Chem. (London)* 16: 81.
- Heuser, E., and A. Scherer
1923. The dry distillation of xylan. *Brenstoff Chem.* 4.
- Jones, J. K. N., C. B. Purves, and T. E. Timell
1961. Constitution of a 4-O-methylglucuronoxylan from the wood of trembling aspen (*Populus tremuloides* Michx.). *Can. J. Chem.* 39: 1059.
- Kitao, K., and Y. Watanabe
1967. Pyrolysis gas chromatography of lignin. *Zairyo* 16(169): 844-847.
- Klason, P., G. Heidenstam, and E. Norlin
1909. Investigations on the carbonization of wood (1) dry distillation of cellulose. *Z. Angew. Chem.* 22: 1205.
- Lipska, A. E., and F. A. Wodley
1968. Isothermal pyrolysis of cellulose. U.S. Nav. Radiol. Def. Lab., NRDL-TR-68-99.
- Loeschcke, V., and H. Franchsen
1964. *Trichocarpin*, a new phenol glucoside from populus bark significant as a resistance fighter. *Naturwissenschaften* 51(6): 140.
- Mack, C. H., and D. J. Donaldson
1967. Effects of bases on the pyrolysis of cotton cellulose. *Textile Res. J.* 37(12): 1063-1071.
- Mehring, K., and W. Schramm
1949. Digestibility of various kinds of cellulose by ruminants. *Turzucht* 1: 11.
- Mojeika, L., and V. Sergeera
1957. Effect of external environmental conditions on the wood cellulose composition of a rapidly growing poplar variety. *Akad. Nauk. Latv., SSSR* 12: 217.

National Fire Protective Association

1967. Fires and fire losses classified 1966. Fire J. 61: 5.

Pearl, I. A., and K. Larson

1965. Studies on the hot water extractives of the brown bark of *Populus trichocarpa*, TAPPI 48(12): 714.

Philpot, C. W.

1970. Influence of mineral content on the pyrolysis of plant materials. Forest Sci. 16(4): 461-471, illus.

Schwenker, R. F., Jr., and L. Beck

1963. Study of the pyrolysis of cellulose by gas chromatography. J. Polytech. Sci., Part C (2). 331 p.

Shafizadeh, F.

1968. Pyrolysis and combustion of cellulosic materials. Pp. 419-474, in Advances in Carbohydrate Chemistry, V. 23, Melville L. Wolfram and R. Stuart Tipson, Ed. New York and London: Acad. Press.

_____, and G. McGinnis

1971. Chemical composition and thermal analysis of cottonwood. Carbohydrate Res. 16: 273-277.

Shimizu, K., F. Teratani, and K. Miyazaki

1968. Effect of the thermal treatment on wood hemicelluloses: II ↑ The change of xylan by heating. J. Japan Wood Res. Soc. 14(7): 376-381, illus.

Tang, W. K., and H. W. Eickner

1968. Effect of inorganic salts on pyrolysis of wood, cellulose, and lignin, determined by differential thermal analysis. USDA Forest Serv. FPL-82, 30 p.

Thompson, J. O., and L. E. Wise

1952. Some molecular properties of the hemicelluloses of big tooth aspen. TAPPI 35: 331.

USDA Forest Service

1967. 1966 forest fire statistics. Div. Coop. Fire Contr., Wash., D.C.

Wodley, F. A.

1969. Pyrolysis products of untreated and flame retardant treated α -cellulose and levoglucosan. U.S. Nav. Radiol. Def. Lab., NRDL-TR-69-B1.

Headquarters for the Intermountain Forest and
Range Experiment Station are in Ogden, Utah.
Field Research Work Units are maintained in:

Boise, Idaho

Bozeman, Montana (in cooperation with
Montana State University)

Logan, Utah (in cooperation with Utah
State University)

Missoula, Montana (in cooperation with
University of Montana)

Moscow, Idaho (in cooperation with the
University of Idaho)

Provo, Utah (in cooperation with Brigham
Young University)

